

PATENT SPECIFICATION
DRAWINGS ATTACHED

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The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are Guenter Poehler, Helmut Giehne, Anton Wegerich and Otto Goehre, citizens of Germany and residents, respectively, of 5, Merzigerstrasse, Ludwigshafen/Rhein, Germany; 88, Friesenheimerstrasse, Ludwigshafen/Rhein, Germany; 15, Kirchenstrasse, Limburgerhof/Pfalz, Germany and 28, Blumenthalstrasse, Heidelberg, Germany.

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COMPLETE SPECIFICATION

Improvements in the Separation of Liquid Mixtures into their Components

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a Joint Stock Company organised under the laws of Germany, of Ludwigshafen on Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 Liquid mixtures which contain difficultly volatile or non-volatile components have hitherto been separated in an evaporator or in a distillation column and the residue thereby obtained collected and periodically exposed to a prolonged treatment at high temperatures. By working in this way, a relatively large proportion of the substances to be separated is decomposed. The residues of substances sensitive to high temperatures and thus liable to decomposition have therefore been worked up in thin layer evaporators in order to separate the remainder of the volatile components. The residues obtained in evaporators or in distillation columns often contain a large amount of volatile components and therefore represent a high fraction of the total volume of the initial liquid mixtures. Because thin-layer evaporators have only a limited capacity it is necessary to employ several of them and this proves uneconomical, time-consuming and troublesome.

10 We have now found that the said liquid mixtures can be worked up most advantageously by introducing them into a distillation column, withdrawing the volatile components at the upper end of said column

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while the less volatile components form, at the lower end of said column, a bottoms product of which the bulk is continually removed and heated to such a temperature in a tube evaporator that a substantial part of the volatile components is vaporised substantially without decomposition, returning at least the vapours formed in said tube evaporator to the distillation column above the level of the bottoms product and supplying a small part of the bottoms product and/or the liquid residue remaining in the tube evaporator to a thin-layer evaporator in which the difficultly volatile or non-volatile components are separated from the volatile components.

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In separating the products of organic synthesis, the residue consists of high boiling point organic substances which may contain nitrogen, oxygen, sulphur and/or halogen. It may also consist of or contain salts which are used in the preparation of the substances.

The process according to the present invention will now be described with reference to the accompanying drawing which illustrates diagrammatically one form of suitable apparatus.

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The initial liquid mixture to be separated is supplied at room or elevated temperature and at atmospheric or reduced pressure to a distillation column 3 which is kept at a temperature which is above the vapourisation point of the portion of the liquid mixture which is to be separated. When separating organic synthesis products of exothermic reactions, it is advantageous to use the heat of the reaction for heating up by heat exchange

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the mixture to be separated before its introduction into the distillation column. The procedure may be that a large proportion of the mixture is vaporised in a preheater 2. 75%, especially 40 to 60%, of difficultly volatile or non-volatile components.

5 While the vapours formed escape from the upper part of the column 3 there flows into the lower part a bottoms product 4 of the non-volatile or difficultly volatile components of the mixture. A large amount of the 70

10 bottoms product, corresponding to the amount of non-volatile components separated from the freshly introduced initial liquid mixture, is removed from the base of the column so that a constant level of liquid bottoms product is maintained in the distillation column. The part removed is led to a tube evaporator 8. In this tube evaporator heating is carried to such an extent that the greater part vaporises without decomposition and the residue remains flowable. The vapours and if desired also part of the residue are returned through a pipe 9 to above the liquid level in the bottom of the distillation column. The circulation between the column 3 and the adjacent tube evaporator 8 can be operated with the aid of a pump 21. Advantageously the column 3 is packed with filler bodies 5 and the vapours ascending in the column 3 vaporise in countercurrent part of the reflux condensate. If the initial liquid mixture is led into the column without preheating, the vapours formed in the tube evaporator and returned to the distillation column may be led in countercurrent to the initial liquid mixture so that it is heated and a part of the same vaporised. 85

15 The liquid residue from the adjacent tube evaporator passes by way of the bottoms product in the column 3 or directly in small batches, for example 0.5 to 20%, with reference to the initial liquid mixture, into a thin-layer evaporator 12 which, if desired, is operated at a lower pressure than the distillation column. It is also possible, however, to supply larger amounts up to 50% of the bottoms product, for example 30 to 40%, to the thin-layer evaporator. The non-volatile components are separated in the thin-layer evaporator. The vapours, preferably in condensed form, can be supplied to the distillation column. 90

20 The temperature of the tube evaporator is preferably so regulated that the level of the liquid bottoms product in the column remains substantially constant and the amount of bottoms product which is removed circulates through the tube evaporator 10 to 100 times per hour. The residue 95

25 concentrating in the tube evaporator, which amounts for example to 0.5 to 30% of the amount of initial liquid mixture supplied to the distillation column, especially 0.5 to 25%, advantageously 1 to 20%, passes, upon return the column 3, into the bottoms product which in general contains 30 to 100

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The larger the amount of the liquid mixture introduced in the distillation column and the larger its content of difficultly volatile and non-volatile components, the greater the amount which must be removed from the bottoms product and vaporised. It is therefore advantageous, to adapt the size of the heating surface of the tube-evaporator and/or the temperature of the tube-evaporator in order to achieve the desired circulation and to keep constant the composition of the bottoms product. It is also possible, however, only to return the vapours produced in the tube evaporator to the column 3, and to collect in the lower part of the tube evaporator a liquid residue which is then supplied to the thin-layer evaporator. It is preferable for a lower pressure to prevail in this thin-layer evaporator than in the distillation column. For this thin-layer evaporator there has proved suitable a downdraught thin-layer evaporator in which the liquid to be vapourised flows down in contact with heated tubes and the vapours formed escape at the top. According to this procedure, the bottoms product in the distillation column is kept at a constant level and a constant composition with 30 to 70%, especially 40 to 60%, of difficultly volatile or non-volatile components. The advantage of working in this way resides in the fact that no great expenditure is required for apparatus and a complete separation of the initial liquid mixture into its components without decomposition can be carried out in continuous operation with small volumetric requirement and high throughput without heat losses and accumulation of residue. The process is suitable for separating into their components crude products of organic syntheses, above all for working up liquid mixtures which contain difficultly volatile and non-volatile components and which in a complete separation into volatile and non-volatile components by the known methods would be decomposed, for example the separation of mixtures obtained by chlorination reactions, nitrogenous organic compounds such as nitriles, the separation of oxidation products of benzene, cyclohexane, naphthalene, heterocyclic compounds and aldehydes and also the separation of reaction products of aniline with water and hydrogen. The process may also be used in the oil industry. The following examples will illustrate further this invention but the invention is not restricted to these examples. Examples 1 and 2 are given with reference to the accompanying drawing:—

EXAMPLE 1.
3200 kilograms of cyclohexanol (which has

been prepared by reaction of aniline with water and hydrogen, has been separated from the reaction mixture and contains about 1% of high boiling point nitrogenous compounds) 5 are supplied per hour through a pipe 1 to a heat exchanger 2 in which it is heated up to 160° C. and 70% of the mixture vaporise. The mixture of vapour and liquid is supplied to a distillation column 3 provided in the 10 central part with filler bodies. The vapours escape from the upper part of the distillation column through a dephlegmator 6 through a pipe 10. At the bottom of the distillation column 3, the liquid part of the initial 15 material collects. About 1100 kilograms per hour of this liquid are led through a pipe 7 into a steam-heated tube-evaporator 8 in which the liquid is heated to 160° C. and extensively vaporised. The vapours and the 20 small unvaporised portion pass through pipe 9 into the distillation column above the level of the liquid. In continuous operation there forms a bottoms product 4 of a constant amount which consists to the extent of 35% 25 of high boiling point nitrogenous compounds and 65% of cyclo-hexanol. The level of the bottoms product is supervised by an automatic level indicator 16 and kept constant by a regulating valve 15. 100 kilograms per 30 hour of liquid are led from the bottoms product through pipe 7 and pipe 11 into a thin-layer evaporator 12 in which the high boiling point substances are separated from the vaporous cyclohexanol. The vapours are 35 introduced through pipe 14 into a condenser 17 and the condensate is then introduced into the distillation column above the level of the liquid, while 32 kilograms of non-vaporisable residue per hour are withdrawn through pipe 40 13.

The cyclohexanol escaping from the distillation column is supplied to a reaction vessel in which it is dehydrogenated to cyclohexanone. The vapours leaving the reaction 45 vessel are supplied to the heat exchanger 2 in which they heat up the cyclohexanol.

EXAMPLE 2.

270 kilograms of a residue, which remains 50 in the steam distillation of the high boiling point reaction product obtained in the reaction of aniline with water and hydrogen, are led through the pipe 1, through the preheater 2 in which they are heated to 90° C., into the upper half of the column 3 provided 55 with filler bodies 5. The liquid components collect at the bottom of the column and form a bottoms product 4. The level of the bottoms product is supervised by an automatic level indicator and kept constant 60 by a regulating valve 15. From the bottoms product 4 a part is continually withdrawn and supplied through the pipe 7 by means of the pump 21 to the steam-heated tube evaporator 8 in which the liquid is heated to 200° C. The vapours formed and the unvaporised part pass at a temperature of 190° C. through the pipe 9 into the column 3 above the level of the liquid bottoms product 4. From the pipe 7, 100 kilograms per hour are withdrawn through the pipe 11 immediately prior to the tube evaporator and supplied to the thin-layer evaporator 12 which is heated with high pressure steam at 20 excess atmospheres. 70 kilograms of this residue, consisting of a nitrogen-free condensation product, are withdrawn per hour through the pipe 13. 30 kilograms per hour of a vaporous product which leaves the thin-layer evaporator at 160° C. through the pipe 14, is condensed in the cooler 17 and the condensate is collected in the vessel 18. The pipe 19 leads to a vacuum pump. The condensate is united with the initial material in the pipe 1 through a pipe 22 by means of the pump 20. They may also be supplied direct to the column 3. A temperature of 155° C. prevails at the top of the column 3. The vapours escape through a dephlegmator 6 through the pipe 10. 200 kilograms per hour of dicyclohexylamine are recovered. The pressure in the column is 25 mm Hg and in the thin-layer evaporator 15 mm Hg.

EXAMPLE 3.

1000 kilograms of crude dichlorbutane which has been prepared from butane-diol and hydrochloric acid are supplied per hour from a preliminary column, in which the first runnings are separated, at a temperature of 80° C. to a column provided with filler bodies. A pressure of 26 torr prevails at the top of the column. The initial material for the most part passes into the bottoms product existing at the bottom of the column. A large part of the bottoms product is continually withdrawn and supplied to a heated tube evaporator with natural circulation, a multiple of the amounts of low volatile material flowing into the column being circulated per unit of time. The heated part is continually returned to the column above the level of the liquid. In the upper part of the column there is a dephlegmator so that part of the distillate flows back into the column as a reflux. 850 kilograms of vapours escape per hour at the top of the column. The liquid level is kept constant at the bottom of the column by withdrawing 150 kilograms of liquid per hour and supplying it to a thin-layer evaporator from which 50 kilograms per hour of a liquid high boiling point product containing chlorine are withdrawn. The vapours escaping from the thin-layer evaporator are condensed. The condensate is returned to the apparatus together with the initial material.

EXAMPLE 4.

1000 kilograms of a crude adipo-di-nitrile which has been prepared from adipic acid

and ammonia are withdrawn per hour at a temperature of 180° C. from a preliminary column and introduced into the middle of a column provided with filler bodies. A pressure of 22 torr prevails at the top of the column. The greater part of the initial material passed into the bottoms product at the bottom of the column. A great part of the bottoms product is continuously withdrawn from the bottom of the column by means of a pump and supplied to a heated tube evaporator. A multiple of the amount of liquid flowing into the column is circulated per unit of time. The heated part is continuously returned to the column above the level of the liquid, the height of which is kept constant. From this circulation, 100 kilograms per hour are withdrawn and led to a thin-layer evaporator. At the bottom of this thin-layer evaporator there are withdrawn per hour 40 kilograms of a high boiling point nitrogenous substance, while the effluent vapours are condensed and supplied to the column in an amount of 60 kilograms per hour with the initial material. At the top of the column there is a diphlegmator so that part of the distillate flows back into the column as a reflux, while 900 kilograms of vapours per hour escape from the column.

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EXAMPLE 5.
Over a container there are situated side by side a downflow tube-evaporator and a distillation column provided with filler bodies. The lower ends of the evaporator and the distillation column are connected to the container. 1000 kilograms per hour of a crude β -naphthol are supplied at a temperature of 160° C. to the distillation column. A pressure of 30 torr prevails at the top of the distillation column. A part of the bottoms product is continually withdrawn from the container and supplied by means of a pump to the upper end of the downflow tube-evaporator. As the liquid flows down, a large part of the same vaporises at the heated surfaces. The mixture of vapour and liquid passes from the lower end of the downflow tube-evaporator into the container. Thence the vapours pass through the distillation column. At the upper end of the same there is situated a diphlegmator. 840 grams of pure β -naphthol escape per hour. 160 kilo-

grams per hour of the bottoms product are supplied from the column to a thin-layer evaporator which operates at 10 torr. From the latter 70 kilograms per hour of liquid residue are withdrawn while 90 kilograms escape as vapour. After condensation of the vapours, the incompletely purified condensate formed can be used for further reactions or supplied to the container again.

In this embodiment it is also possible to use a container over which is situated only the downflow tube-evaporator, while the distillation column is connected to the upper part of the tube-evaporator. In this arrangement, the vapours from the downflow tube-evaporator flow directly into the distillation column, while the non-vapourised liquid flows into the container.

WHAT WE CLAIM IS:—

1. A process for separating into its components, a liquid mixture which contains difficultly volatile or non-volatile components by vaporisation and fractional distillation, wherein the liquid mixture is introduced into a distillation column, the volatile components are withdrawn at the upper end of the column while the less volatile liquid components form a bottoms product from which the bulk is continually withdrawn and heated in a tube evaporator to such a temperature that a substantial part of the volatile components is vaporised substantially without decomposition, returning at least the vapours formed in the tube evaporator to the distillation column above the level of the bottoms product and supplying a small part of the bottoms product and/or the liquid residue remaining in the tube evaporator to a thin-layer evaporator in which the difficultly volatile or non-volatile components are separated from the volatile components.

2. The process for separating liquid mixtures into their components substantially as described in any of the foregoing examples.

3. Apparatus for separating liquid mixtures into their components substantially as herein described with reference to the accompanying drawing.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Chartered Patent Agents,
Agents for the Applicants.

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1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

